



Photoemission study of Silicon with TEMPO beamline at Soleil

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Nanomat Master Program – Group 2
Thursday, November 17th 2011

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Introduction

X-Ray photoelectron spectroscopy (XPS) is an extremely powerful technique, designed for the identification of chemical species, chemical and electronic states of the constitutive elements of any kind of material. High energetic photons can notably access the core levels of electrons which are specific of the analysed system, giving thus precise information on the present atoms or molecules. If carefully treated, the obtained data can give even more information, such as chemical shifts, vibrational fine structure, surface reconstruction, all relatively related to the chemical environment which can thus also be investigated. However, the data treatment in XPS is not trivial. In this report we present the main aspects of this technique based on Si (100) experiments done at TEMPO beamline of SOLEIL synchrotron, in Saclay. We present briefly the basic principles of XPS measurements and how synchrotron radiation is different from laboratory sources. Then, we show and discuss our results of the study on silicon surface, when rough, clean and finally covered with adsorbate with a time resolved approach.

1 Basic principles

Based on the photoelectric effect, photons can knock out electrons out of a given material, if the photon energy $\hbar\omega$ is higher than the workfunction Φ of the material. The kinetic energy E_{kin} of the ejected electrons depends on their binding energy E_{B} such that:

$$E_{\text{kin}} = \hbar\omega - E_{\text{B}} - \Phi \quad (1)$$

It is this simple equation, on which photoelectron spectroscopy is all based on. The principle is to shine light of a given energy on the sample and then analyse the kinetic energy of the ejected electrons. In XPS, the energy of the incident photon is high enough to access the core-levels of the atoms. The typical photon sources in a laboratory uses the K_{α} and K_{β} emission lines of aluminium and magnesium anodes. These sources have the disadvantage that firstly we do not only get these discrete energies, but also their satellites and a broad bremsstrahlung spectrum and secondly they usually operate at very low power, providing low intensity sometimes insufficient to excite core levels. Synchrotron radiation on the other hand can be very accurately tuned in energy and the flux of photons is enormous, being thus a perfect monochromatic photon source for XPS experiments.

Synchrotron radiation is based on the principle of light emission due to acceleration of charged particles moving at a velocity close to the speed of light. In the beamline of this experiment, so called undulators are used to generate a photon beam at a specific energy. An undulator basically consists in a periodical series of aligned alternate magnets. Contrary to other insertion devices such as bending magnets, which bend the trajectory of the electrons while accelerating them, thus generating a unique synchrotron radiation event tangent to this bent direction, the undulators induce a wiggling of the electron movement by applying an alternating magnetic field, which generates synchrotron radiation at each oscillation of the electrons. Therefore, between each element of the series of alternative magnets, radiation adds up forming a very bright and intense radiation, with high brilliance¹ in the direction of propagation of the electrons. Usually, linear polarization of light

¹TEMPO beamline is optimized to provide maximal brilliance for photon of energy between 0.2 and 2 keV.

is obtained, from lateral oscillations of electrons between the magnets. The energy of the produced photons can be modified by increasing the magnetic field in the undulator by varying mechanically the gap between the magnets. Together with a monochromator, the photon beam energy can therefore be precisely defined.

The set-up used for this experiment is set at the end of one of the numerous beam lines. A ultra high vacuum chamber with a pressure of about 10^{-10} mbar is required first of all to get rid of sample contamination and maintain clean sample surfaces and second of all to ensure collision-free and durable analysis with the analyser. The analyser works as follows: retarding and acceleration lenses, combined with an entrance slit, define an energy window around a chosen pass energy E_{pass} , which is kept constant at low energy values for high resolution purposes. Electrons with a certain energy enter a hemispherical electric field and are bent due to their kinetic energy. The passing electrons are then counted by a position sensitive micro-channel plate coupled with a delay line detector, giving access to both the emission angle and the kinetic energy of the electron within the energy window. In order to get rid of the spatial inhomogeneities in the detector response, responsible of non-linearity of count rates inducing distortions of the spectra, the detector processes in sweep mode. Within a certain energy window, the entry lenses move (sweep) in order, for each point of a spectrum, to be measured by the whole detector. The final swept spectrum is finally calculated by a computer.

2 An overview of rough Silicon surface

2.1 Photoemission processes

We start our measurements with an overview of rough surface of a Si (100) sample. Two measurements are performed at a pass energy $E_{\text{pass}} = 50$ eV with incident photon energy $\hbar\omega = 680$ eV and $\hbar\omega = 700$ eV. The two spectra which correspond to the count rate of photoelectrons as a function of their kinetic energy are superimposed in figure 1, and table 1 sums up the collected data.

One observes that some parts of these two spectra coincide while some of the sharp peaks are shifted at higher energy (+20 eV) for incident photon energy of 700 eV. According to equation 1, the kinetic energy of the photoelectrons changes with changing photon energy. The shift of the peaks therefore corresponds to the difference of photon energy of the two experiment. However, the steady parts of the spectra corresponds to photoelectrons for which the kinetic energy is independent from the excitation source. Such collected electrons are indeed Auger electrons, which originate from so-called Auger transitions. When a core-hole is created due to the excitation of a core-level electron in, let say, an electronic shell K leaving the atom in an excited state, an electron of a higher shell L relaxes to the inner excited shell together with the emission of a photon. The energy of this photon is equal to the difference of energy between the level K and L . This photon can then excite an electron of a higher shell M which may leave the atom in an ionized state. This lastly emitted electron is the Auger electron and its kinetic energy is strictly dependent on the binding energies of the electronic levels of the excited atom, and not on the original photon energy which creates the initial core-hole at the origin of the Auger transition described above. Exciting the sample with two photon energies thus allows to distinguish between photoelectrons and Auger electrons. Comparing the peaks

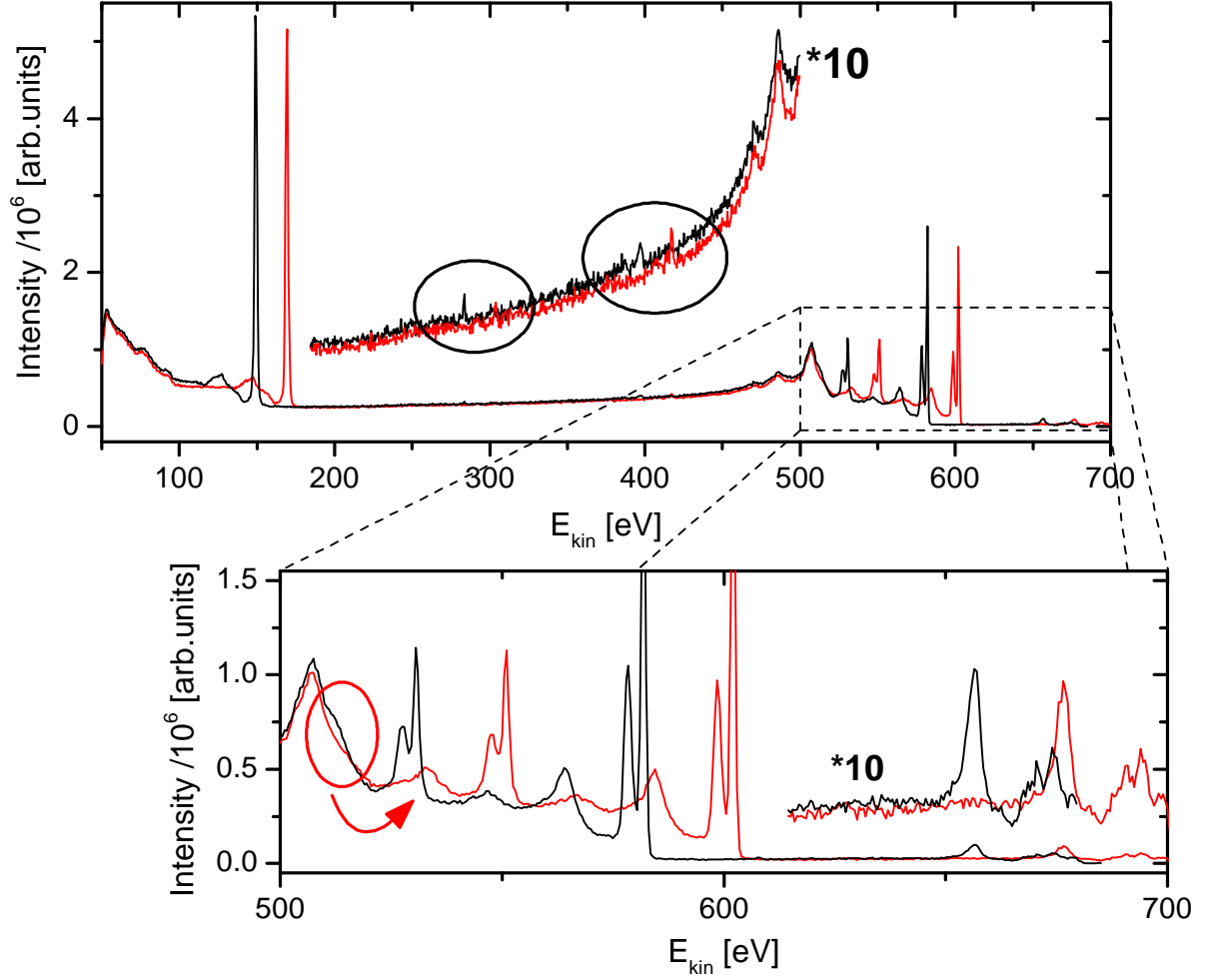


Figure 1: Overview spectrum of Si (100) recorded at two different photon energies, $\hbar\omega = 680$ eV (black) and 700 eV (red). Some of the peaks are shifted, when tuning the photon energy, corresponding to true core-level electrons, whereas the steady peaks reveal the Auger electrons. Magnifications are shown in order to illustrate each peak.

to literature values [1] it is possible to assign them to the different physical origin.

We can see a drop of intensity on the onset of the graph at low kinetic energies. This is the tail of the secondary electron peak, that contains all electrons, that have lost the information on their physical origin by scattering and losing kinetic energy when moving through the sample towards the surface. This gives in general a very broad and intense peak at low energies, that can affect the observed spectrum. The secondary electron peak is not shifted, when changing the photon energy. It also contains some oscillations, that cannot be assigned as the corresponding binding energy (more than 600 eV) would be higher than the ones of the atoms and molecules that could be present in the chamber and on the sample. Therefore, they must belong to the secondary electrons as well.

2.2 Identification of the different peaks

In this section, we discuss qualitatively the nature of the peaks and their origin in terms of atomic electronic level. One uses the set photon energies (700 and 680 eV) as the correct

ones but we will show in section 4 on page 8 how to measure with a dispersive method the effective photon energy imposed to the sample, which is slightly modulated by the optics and the set-up.

At 169.5 eV on the red line, we can see a huge narrow peak. The same is observed on the black line at around 150 eV. The shift between the two peaks is around 20 eV, which corresponds to the difference of the two incident photon energies. The corresponding binding energy value of 531 eV is close to the one of the oxygen 1s level at 543.1 eV. However, the accuracy of XPS is much higher than this observed disagreement of about 12 eV, as we will see in the following. So this difference must have a physical origin. And indeed, if we consider that oxygen atoms are bond to surface silicon thanks to the presence of water molecules H_2O in the analysis chamber, given the higher electronegativity of the former over the latter, it turns out that core-levels of oxygen are shifted towards lower binding energy. In a simple picture, the electrons involved in the Si-O covalent bond are much more attracted towards oxygen which slightly gains charge and therefore its core electrons are more alike to be excited, due to an overall excess of electrons, and their binding energy decreases. The gain and loss of negative charge within the Si-O covalent bond for O and Si is represented by the partial charge δ^- and δ^+ respectively. These considerations about the core-level binding energy shift of O 1s are related to the environment of the oxygen atoms when probed by X-Rays, that is to say to the initial state of the photoemission process. Further considerations can arise regarding the final state of the PE process. A core-hole can be more or less screened by outer electrons which ensures an increase in extra-atomic relaxation energy of the core-hole. Such an increase leads to a decrease of the binding energy of the corresponding core-level electrons. This might be taken into account when trying to understand the low values of binding energy of oxygen with respect to its environment. The two magnified peaks at very high kinetic energies, for which the spectra have been multiplied by ten, correspond to weakly bond electrons of binding energy 23.5 eV. The closest binding energy found and compatible with the present atoms in the chamber is 41.6 eV of O 2s. In analogy with the above mentioned core-level shift, same reasoning suggests that valence electrons of highly electronegative atoms are shifted to lower binding energy when involved in the bonding with a less electronegative ligands such as silicon. The last peak at a measured binding energy of around 6 eV could be assigned to H 1s. The reason for this is that it is the smallest binding energy possible. However, this is inconsistent with the fact that an atom bound to an element which is more electronegative undergoes core-level shifts to higher binding energy. Either for hydrogen this statement can not be used, or this peak at very low binding energy does not correspond to hydrogen.

Other tiny peaks are noticed at around 300 and 400 eV and are circled on figure 1 on the main curves of ten times higher intensity displayed above the spectra. The fact that the peaks show up on both spectra with each times a shift of 20 eV attests that they originate from core electrons that were kicked out from atoms with photons of same energy difference. A comparison to literature values [1] associates the photoelectron at a kinetic energy 417 eV (red line) with a carbon 1s electron of binding energy 283 eV. The very small peak at a binding energy of 396 eV can be assigned to N 1s core-level (nitrogen) whose binding energy is found in literature at around 410 eV.

Contrary to oxygen which may be present either in vapour or adsorbed on the surface

of silicon and which is always bond to less electronegative atoms than itself (i.e. hydrogen or silicon atoms), silicon can be found in two very distinct oxidation states whether it is bond to other silicon atoms in the bulk of the sample or to the above mentioned adsorbed water molecules. On the magnified part of figure 1, the doublet corresponding to photoelectrons of binding energy 98 eV and 101.5 eV (e.g. the doublet around 600 eV for the red line) correspond to core-levels of Si 2p and $\text{Si}^{4\delta+}$ 2p core-electrons respectively. Same observation is made for the doublet that gives two close peaks at 551 and 547.5 eV, where the highest one is related to the 0th oxidation state of silicon while the smallest one at higher binding energy corresponds to $\text{Si}^{4\delta+}$ 2s core-electron. For both oxidation states of 2p and 2s levels, the core-level shift is 3.5 eV which is consistent with published measured and calculated values [2].

Furthermore, other notable information can be extracted from figure 1. Satellites at lower kinetic energy are observed on the left of almost every peaks, periodically positioned and with decreasing intensity. Looking at the red line, the peaks at 584.5 and 567 eV are shifted from the Si 2p peak, taken at 602 eV and discussed previously, by 17.5 and $2 \cdot 17.5 = 35$ eV. The same energy shift (around 18 eV) can be seen between Si 2s peak and the bump pointed by the red arrow. This red arrow illustrates this shift that also can be observed for the spectrum of $\hbar\omega = 680$ eV (black line) thanks to the small bump on the right part of the broad peak of Auger electrons, on the very left of the magnified spectrum.

These regular satellites at lower kinetic energy corresponding to photoelectrons which have loss an apparently quantized amount of energy are the signature of plasmon losses. The photoemitted electrons loose energy in favor of collective valence band electron excitations. In the same way as phonons are quantizations of mechanical vibrations, plasmons are quantizations of the oscillations of electronic clouds of atoms (plasma oscillations). A plasmon peak for oxygen 2s is also thought to be at a binding energy of 552.5 eV, corresponding to a loss of energy for the $\text{O}^{2\delta-}$ 1s photoelectron of about 22 eV. One sees that the plasmon energy is higher for oxygen compared to silicon. This might be due to the higher valence electron density around oxygen since it is highly electronegative. The plasmon peaks are reported in table 1, for the two first observed orders (I and II).

3 Si 2p core-levels of bulk and surface Si (100)

The overview measurements of section 2 on page 2 gives great insight of how rich a photoemission spectrum can be, in terms of qualitative chemical analysis. Higher resolution study can give even more information and lead to accurate description of intrinsic quantum effects and microscopic phenomena and interactions that occur at the surface of the sample.

3.1 XPS sensitivity of surface and bulk

The second set of measurements were performed with two very distinct incident photon energies. On the one hand, we used photons of energy 700 eV and on the other hand photons of energy 150 eV. Two cases can be distinguished, whether we are probing bulk or surface atoms with the chosen incident flux of photons. To argue this, one considers that the photoemitted electrons after photoexcitation from a bound state towards a free

$E_K^{(680)}$	$E_K^{(700)}$	$E_B^{(680)}$	$E_B^{(700)}$	E_B^ℓ	Photoelectron origin
127.5	147.5	552.5	552.5		O ^{2δ-} 1s (I)
149	169.5	531	530.5	543.1	O ^{2δ-} 1s
283.5	304	396.5	396	409.9	N 1s
397	417	283	283	284.2	C 1s
512.5	532.5	167.5	167.5		Si 2s (I)
527.5	547.5	152.5	152.5		Si ^{4δ+} 2s
530.5	551	149.5	149	149.7	Si 2s
546.5	567	133.5	133		Si 2p (II)
564	584.5	116	115.5		Si 2p (I)
578.5	598.5	101.5	101.5		Si ^{4δ+} 2p
582	602	98	98	99.62	Si 2p
656.5	676.5	23.5	23.5	41.6	O ^{2δ-} 2s
674	694	6	6	13.6	H 1s

Table 1: Kinetic and binding energies of the collected photoelectron after the XPS experiment on rough Si (100) surface. The data are shown along the corresponding literature values E_B^ℓ . For each photoelectron, the corresponding physical origin is proposed, according to literature and to the chemical environment and interactions in the sample chamber.

state of the continuum are subjected to inelastic scattering. The inelastic losses with other electrons are characterized by a the so-called *inelastic mean free path* (IMFP) λ , which is an index of how far an electron can travel through a solid before losing energy. The kinetic energy of the emitted electrons is damped by a factor $e^{-d/\lambda}$ where d is the crossed layer thickness. This factor stands for the probability of the electrons to travel the distance d without undergoing inelastic scattering. It has been stated that the measured monokinetic electrons of energy $E_K \simeq 50$ eV are electrons with the lowest IMFP, that is to say with the lowest escape depth from the sample. Such electrons are therefore more likely coming from surface atoms. Very much slower photoemitted electrons ($E_K \ll 50$ eV) have underwent a lot of inelastic scattering and hence originate from deep bulk atoms. On the contrary, higher photon energy probe both bulk and surface. Subsequently, one shall choose the correct excitation energy $\hbar\omega$ whether one wants to obtain kinetic energy of photoelectrons in the range of surface or bulk sensitivity. For example, for a given probed core-level of known binding energy, say $E_B(\text{Si } 2p) \simeq 100$ eV, one thus chooses to use photons at $\hbar\omega = 150$ eV in order to collect photoelectrons of kinetic energy around 50 eV with a view to actually probing electrons with the minimal IMFP and hence being mostly surface sensitive.

Figure 2 depicts exactly that kind of experiment, where the Si 2p levels have been excited either with photons of energy 700 eV (2a) or 150 eV (2b). On both spectra, one observes two main peaks, one broad peak and one doublet at higher kinetic energy, which corresponds to photoelectrons of binding energy 98 and 101.5 eV respectively. One sees that for photon energy $\hbar\omega = 150$ eV, the doublet almost totally extinguishes whereas the broad peak keeps the same intensity. According to the data presented in table 1, the broad and less intense peak on both spectra at a binding energy of 101.5 eV corresponds to a 2p core-level of silicon in its 4+ oxidation state, while the doublet whose highest component is centred at a binding energy of 98 eV represents Si 2p core-level. Based upon this and enlightened by the arguments opening this section about depth sensitivity

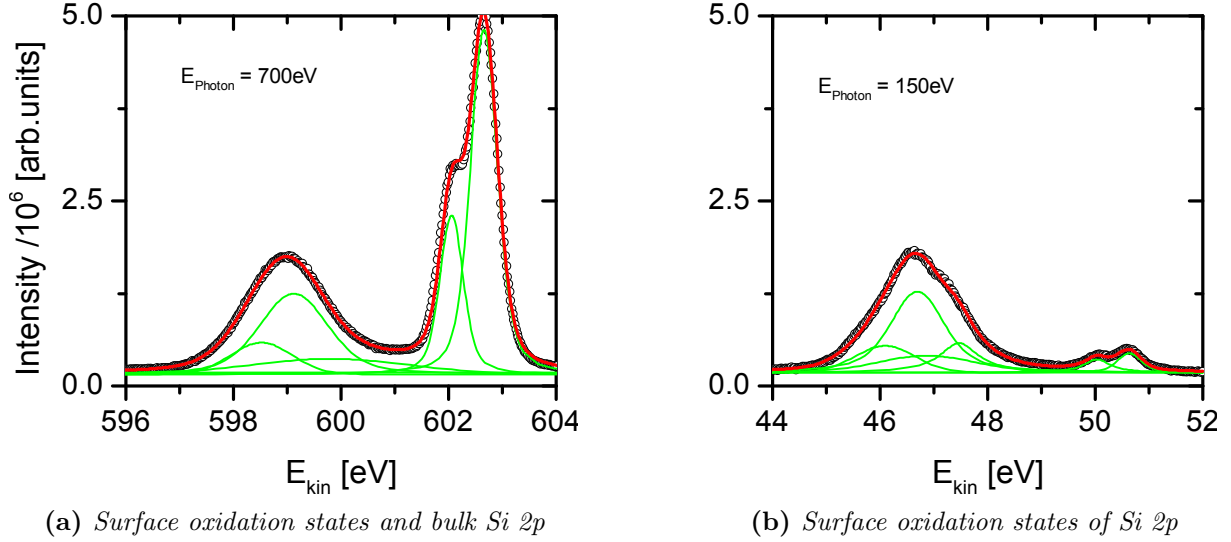


Figure 2: Photoemission spectra of core-level Si 2p with two very different photon incident energy, $\hbar\omega = 700$ eV on figure 2a and $\hbar\omega = 150$ eV on figure 2a. The black circles are the data, the green lines are the fitted peaks using Voigt profiles and the red line is the overall fitted curve.

of XPS, figure 2b shows high surface sensitivity whereas figure 2a obtained with photon energy 700 eV shows both bulk and surface sensitivity. A close look at the surface sensitive spectrum and the broad peak shows a bump at a kinetic energy of around 47 eV. This corresponds to a photoelectron of binding energy higher than Si 2p but lower than $\text{Si}^{4\delta+}$. It is indeed an intermediate oxidation state, with a core-level shift of approximately 2.5 eV and corresponding to Si 3+ oxidation state. Also, the shift in binding energy for the 4+ oxidation state is consistent with the measured values by F. J. Himpsel *et al.* [3] of around 3.6 eV. Consistently with this paper, our measurement gives great insight on the chemical environment of silicon: surface $\text{Si}^{4\delta+}$ are bond to four oxygen ligands as in SiO_2 and $\text{Si}^{3\delta+}$ are bond to three oxygen ligands and one silicon, as in the Si – SiO_2 interface. Further investigations, namely comparing the relative intensity of the peaks, could give information on the thickness of the supposed oxide layer on the surface of the sample. Our fitting procedures did not totally allow us to perform a complete deconvolution of all the supposed peaks. Although we kept some core-level shifts constant (such as the spin-orbit splitting and the relative intensity of the peaks as well as and the oxidation states positions), some embedded peaks, namely the 3+ oxidation state, could unfortunately not be resolved by fitting. Lastly, one sees that the overall broadening of the oxidation states peaks is larger than the one of neutral Si 2p. This can be related to a smaller lifetime of the oxidation state as the surface of the sample is the most reactive location on the sample, where water binds to surface silicon.

3.2 Spin-orbit splitting

Together with the information of the chemical environment, this close look at the Si 2p core-levels shows a quantum effect based on the nature of the electrons which are Fermions: their spin. In spectroscopy, the state of an electron can be given by the so-called *term symbol* which writes $^{2S+1}L_J$ where L is the total orbital momentum, S is the spin and $J = |L \pm S|$ is the total angular momentum of the electron. The possible electronic states

for such values of L , S and J are given by the main total angular momentum which goes from $|L - S|$ to $L + S$ in integer steps (that is to say $1/2$ and $3/2$ in the case of silicon). Hund's rules predict that for more than half filled subshell (which is the case for the 2p orbital), the level of highest J is the lowest in energy. Hence, in the case of an Si 2p electron whose spin is $1/2$ and total orbital momentum $L = 2$, the state of lowest energy has a total orbital momentum $J = L + S = 3/2$. The so called spin-orbit coupling lifts the degeneracy of the 2p states in such a way that the state written $2p_{3/2}$ of $J = 3/2$ is lower in energy than the state $2p_{1/2}$ of $J = 1/2$. This splitting can be observed if the resolution is high enough and, in such a way that $2p_{3/2}$ lies at higher kinetic energy, i.e. lower binding energy than $2p_{1/2}$. The relative intensity between both are expected to follow the ratio $\frac{2 \cdot 3/2 + 1}{2 \cdot 1/2 + 1}$, which is what we observe on figure 2a.

4 Measure of the actual photon energy

The synchrotron light used for the experiment is tuned and its energy and polarization can be chosen as will. However, it remains a slight difference between the set value of photon energy and the one actually hitting the sample for photoexcitation. In order to know the actual X-Ray energy, one uses two elements of the set-up: the undulators and the monochromator. As presented in section 1 on page 1, the gap between the undulator can be tuned, providing a control of the magnetic field that affects the electrons' oscillating motion and therefore the generated synchrotron radiation energy. Even though it is already highly monochromatic, light passes through a dispersive monochromator which is oriented at a chosen angle in such a way that the first order Bragg peak at a chosen monochromatic energy is directed straightly onto the sample. A couple of measurements are done from which the value of the photon energy at the beginning of the beamline is deduced. First we set the undulator gap in such a way that photons of energy 150 eV are generated to probe the Si 2p core-levels. Then, we choose an other gap distance, which generates photons of energy compatible with second order diffraction on the fixed monochromator, according to Bragg law, and collect once more the photoemission of Si 2p. Figure 3 shows the two spectra obtained with light coming from first order (3a) and second order (3b) diffraction. The difference in kinetic energy of the photoelectrons coming from the same core-levels of equal binding energy gives the exact value of the photon energy. It is averaged over the two pairs of spin-orbit split peaks and is equal to $\hbar\omega = 149.8938$ eV.

5 Measure of the workfunction

The possibility for a photoelectron to escape from matter, that is to say the ionization of a constitutive atom, is not determined only by its inelastic mean free path as presented in section 3.1. As a matter of fact, the removed electrons have to overcome a potential barrier originating from the states at the surface of the material, the so-called *workfunction*. It can be defined as the difference in energy between the vacuum level and the Fermi level of the material. As it appears in equation 1 on section 1 on page 1, the kinetic energy of the photoelectrons depends constitutively on the binding energy and on the workfunction of the material. The photoelectrons measured with the highest kinetic energy are those at highest energy state in the material so that the slightest kick remove them from the sample. They actually lie at the *Fermi level* of the material and have a kinetic energy, with respect

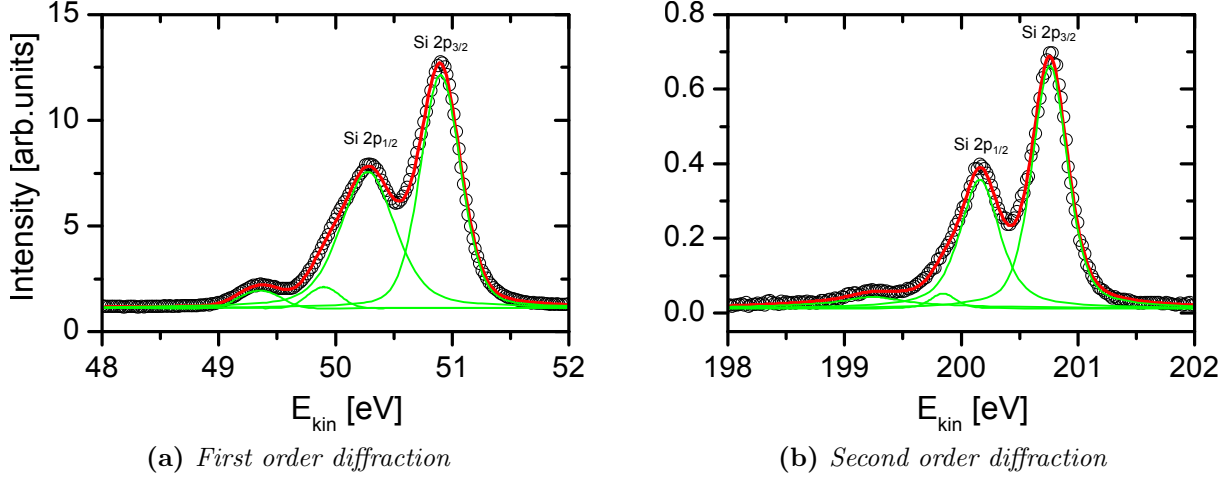


Figure 3: Photoemission spectra of Si 2p core-levels with two different photon energy corresponding to the first and second order diffraction of an incident beam of energy $\hbar\omega$.

to the Fermi level, noted $E_{\text{FermiEdge}}$. Oppositely, the slowest measured photoelectrons escape the sample with just enough kinetic energy to overcome both the workfunction of the sample Φ_{sample} and the one of the analyser Φ_{analyser} they reach. These electrons correspond to the secondary electrons which have scattered inelastically on their way out of the sample. They have a *cut-off* kinetic energy, with respect to the Fermi level, E_{CutOff} which is the lowest kinetic energy measured and is the onset of a photoemission spectrum. A definition of the sample workfunction is given in the following expression:

$$\Phi_{\text{sample}} = \hbar\omega - E_{\text{FermiEdge}} + E_{\text{CutOff}} \quad (2)$$

In order to be detected, the kinetic energy of photoelectrons reaching the analyser has to be high enough to pass the workfunction of the analyser. Also, in order to be sure to detect the slowest photoelectrons, the material under study is polarised by a voltage bias which shifts up the ground state energy. A bias $V_{\text{bias}} = 10$ V is applied such that the whole spectrum is shifted up by 10 eV which makes certain the detection of the cut-off photoelectrons. This bias indeed shifts up all the energy levels of the sample, from the Fermi level to the vacuum level, and therefore the workfunction of the sample.

Figure 4 illustrates the cut-off and the Fermi-edge parts of a photoemission spectrum performed with photon energy $\hbar\omega = 149.894$ eV and a bias voltage $V_{\text{bias}} = 10$ V. The bottom part presents a scheme of the above mentioned quantities with respect to the Fermi level of the sample. Plugging the measured values into equation 2 provides a workfunction value of $\Phi_{\text{sample}} = 5.654$ eV.

6 Surface reconstruction of clean Si(100)

Even though the sample is studied in ultra-high vacuum, some gas species remain in the chamber, mainly water as discussed in section 2.2 when traces of oxygen have been shown, as well as in section 3.1 when we discussed the surface sensitivity and the bonding of water on surface silicon atoms. Therefore, one can reasonably wonder how the core-levels are observed on a cleaned surface. To clean the sample, one heats it up, up to

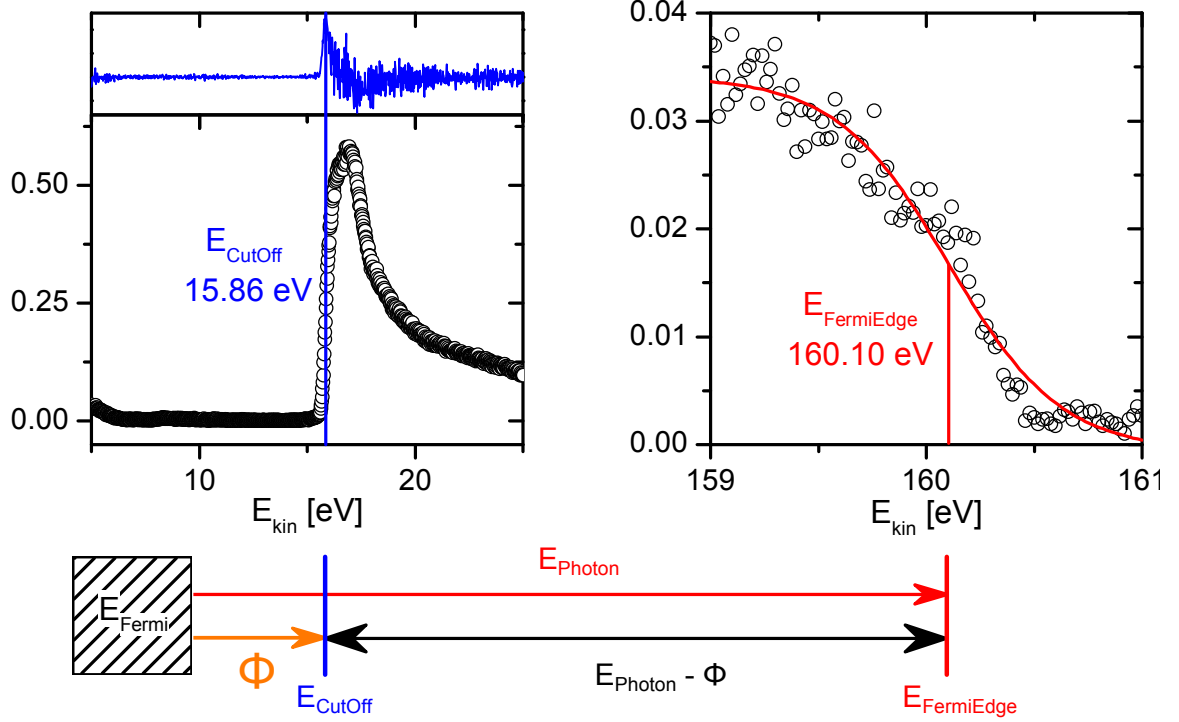


Figure 4: Cut-off kinetic energy and energy of the Fermi-edge of the photoemission spectrum of silicon with photon energy $\hbar\omega = 149.894$ eV and voltage bias $V_{bias} = 10$ V. The bottom part shows the relative positions of the involved quantities with respect to the Fermi level of the material.

more than 1000°C thanks to a 10 A current running through it for a few seconds. An optical pyrometer is used to measure the temperature of the heated sample by observing it through one of the chamber's windows.

Right after it is cleaned, a Si 2p photoemission spectrum with photon energy $\hbar\omega = 150$ eV is acquired and is now depicted in figure 5. We can see the bulk Si 2p doublet and an additional shoulder at lower binding energy. Since the surface is cleaned, surface silicon atoms are supposed to be free from any water molecule. It is known that the structure of the surface (100) of silicon shows two dangling bonds per surface atoms. These dangling bonds reconstruct by pairs forming dimers, leading to the buckling of the surface atomic layers. The surface is thought to reconstruct in such a way that silicon electron rich atoms form summits of a buckled layer. Since this experiment is very much surface sensitive, the observed core-level shift hence can be assigned to surface silicon atoms whose core-level states are slightly less bonded because of the rich electronic density around these atoms. The interpretation of these surface silicon atoms free from water is extended in the following section in a time-resolved photoemission experiment.

7 Time resolved photoemission: study of water contamination

In this last section, we present a photoemission experiment extended in time, in the sense that photoemission spectra are acquired regularly and a study of their variation and evolution is made. One focuses on the Si 2p core-level and the evolution of the surface states when exposed to the remaining water. The photoemission spectra are presented

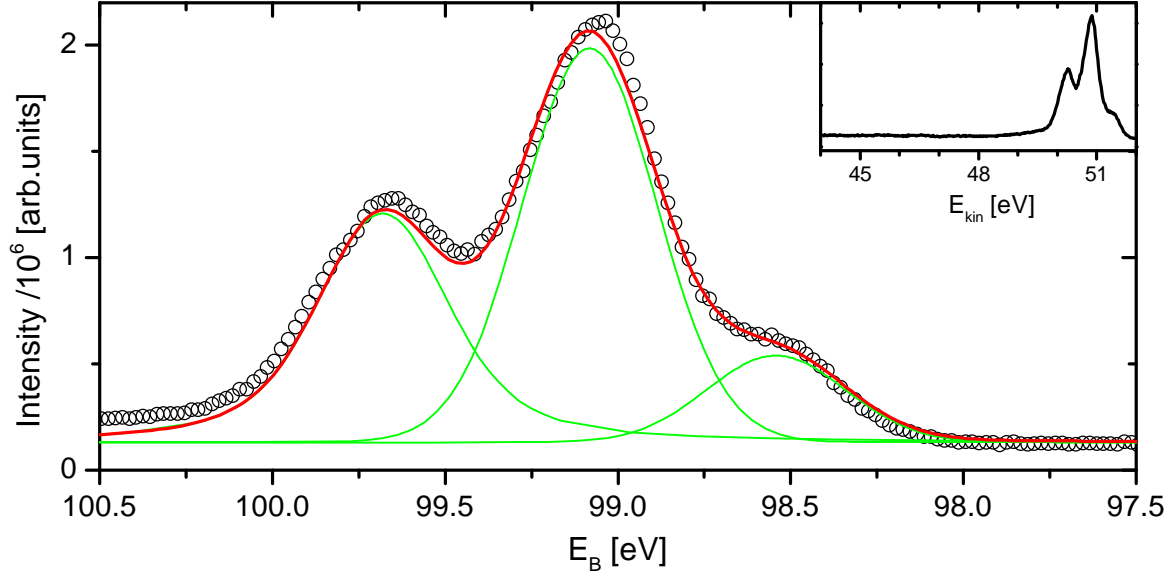


Figure 5: Photoemission spectrum of Si 2p core-level with photon energy $\hbar\omega = 149.894$ eV right after cleaning by heating. Data are the black circles, green lines are Voigt fitting peaks and the red line is the overall fit. This spectrum shows the bulk Si $2p_{3/2}$ (highest peak at $E_B = 99.09$ eV) and Si $2p_{1/2}$ (smaller peak at $E_B = 99.67$ eV) components. The additional peak at lower binding energy at around $E_B = 98.5$ eV corresponds to the core-level electrons of surface silicon atoms which undergo dimerisation reconstruction.

in figure 6. Both pictures show the intensity as a function of binding energy of the photoelectrons. Twenty photoemission scans have been performed approximately every minute. They are depicted on a color scale graph on the left showing the intensity in arbitrary unit, maximum being 2. The graph on the right illustrates the evolution of the surface Si 2p in a water fall diagram, in which the bottom and top curves are the first and last scans respectively. Both pictures hence show the evolution in time of the Si 2p core-level.

The first scan is performed after having cleaned the sample and is pretty much similar to the photoemission spectrum shown in figure 5 of clean surface Si 2p. Firstly, one observes that this peak decreases down to vanishing after a few scans. At the same time, a small bump appears and increases at higher binding energy, higher than the binding energy of Si 2p. Knowing that the sample surface is exposed to water, the observation of the decrease of the peak characteristic to the clean surface (as described in the previous section 6) allows us to say that silicon surface is affected by water. Among the well-known core-level shifts, an atom involved in a covalent bond with species more electronegative has its core-level shifted to higher binding energy. This initial-state shift is indeed observed in this experiment: the signal at higher binding energy corresponds to surface silicon bond to water molecules, as it is described and discussed in section 3.1 about surface sensitivity.

A close look at the intensity and broadening on the color scale diagram shows a variation in the main Si 2p peak. It seems to get thinner as time passes. The decrease in the broadening can be interpreted as an increase of lifetime, as the sample tends to reach an equilibrium state after it has underwent a strong heating.

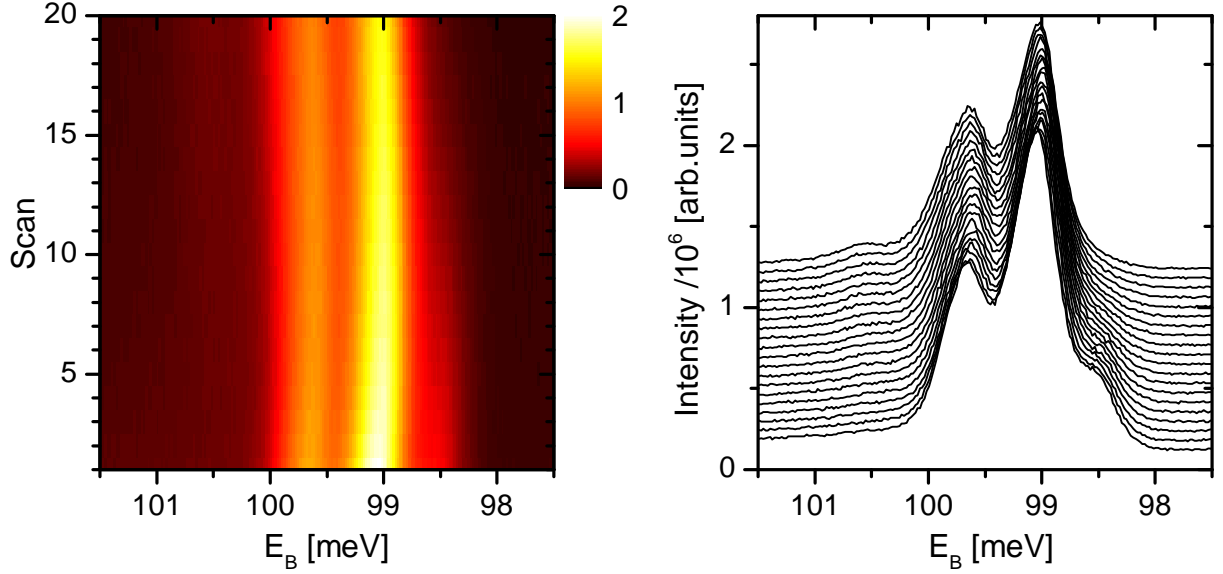


Figure 6: *Time-resolved photoemission spectra of Si 2p core-levels with photon energy $\hbar\omega \simeq 150$ eV. 20 spectra are performed, each of them demanding around 45 seconds. On the left, the higher the scan index, the longer time has elapsed. On the right, the first scan is at the bottom while the last one is on top.*

Conclusion

This practical has given us the opportunity to perform X-Ray photoemission spectroscopy with an internationally used and state-of-the-art experimental set-up and has shown how powerful and highly accurate this technique is. Changing very few experimental parameters offered to resolve core-levels with chemical and physical specificity. The sample under investigation could be studied either in its bulk or at its surface providing both very instructive and highly resolved pieces of information on both its chemistry and physics. Having the chance to work in such an advanced platform which is a true principal focus for modern science makes us very thankful and very much looking forward to being able to use it again in a near future.

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